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FLAT-PLATE SOLAR ARRAY PROJECT
PROCESS DEVELOPMENT AREA
PROCESS RESEARCH OF NON-CZ SILICON MATERIAL

QUARTERLY REPORT NO. 5

APRIL 1, 1985 - June 30, 1985

CONTRACT NO. 956616 - Mod. 1

July 1985

The JPL Flat-Plate Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

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TECHNICAL CONTENT STATEMENT

A. CONTRACT GOALS AND OBJECTIVES

The program goals for this contract modification are as follows:

- Investigate excimer-laser drive of liquid dopants to form front and back junctions on dendritic web silicon.

  (a) Conduct process sensitivity studies to optimize laser drive-in parameters such as energy density (J/cm^2), pulse duration (secs), pulse overlap (%), and rep-rate (pulses/sec). The excimer laser processing will be carried out by Spectra Technology, Bellevue, WA, under a subcontract from Westinghouse.

  (b) The liquid dopants to be used in the laser drive investigation shall include phosphorus, boron, and aluminum.

  (c) Both N type and P type dendritic web material will be used in the laser drive-in investigation.

- Perform cost analyses on the laser drive-in junction formation process using IPEG (Interim Price Estimation Guidelines) methodology. SAMICS Format A's will be filled out on the laser drive process and submitted to JPL.

- Twenty-four (24) sample solar cells and 200 inches of dendritic web material will be provided to JPL.

In addition to these goals, several experiments were carried out using a unique method for simultaneously diffusing the solar cell junctions.

B. SUMMARY

This report describes work performed on JPL Contract 956616-Mod. 1 during the period from April 1, 1985 through June 30, 1985.

During the program, three sets of samples have been laser processed at Spectra Technology and returned to Westinghouse for cell processing. The laser processing has been carried out on P-type and N-type web at laser power levels from 0.5 joule/cm^2 to 2.5 joule/cm^2. Six different liquid dopants have been tested (3 phosphorus dopants, 2 boron dopants, 1 aluminum dopant). The laser processed web strips have been fabricated into solar cells immediately after laser processing and after various annealing cycles.

Spreading resistance measurements made on a number of these samples indicate that the N^+P (phosphorus doped) junction is ~ 0.2μm deep and suitable for solar cells. However, the P^+N (or P^+P) junction is very shallow (<0.1μ m) with a low surface concentration and resulting high resistance.

Due to this effect, the fabricated cells are of low efficiency. The maximum efficiency attained was 9.6% on P-type web after a 700°C anneal. The main reason for the low efficiency was a high series resistance in the cell due to a high resistance back contact.

A second, novel, technique for simultaneous junction formation has been studied in the last several months of the program. This method uses a high intensity flash lamp which heats the dendritic web (both sides coated with a dopant glass) to a high temperature for a short period of time. Initial data on cells fabricated on this method show promising results.

C. TECHNICAL PROGRESS

C.1 Laser Processed Samples

The last (third) set of laser processed samples were fabricated into solar cells during this period. Both junctions on these cells were formed by the laser drive method.*

This sample set contained web strips with either an Al dopant or a boron dopant on the back. All strips had P-100 as the phosphorus dopant on the front. The laser power used for drive-in was also increased in this test. No problems were experienced by Spectra Technology during the processing.

Figures 1 and 2 show spreading resistance data on Web Crystal #52-2. This data is representative of several other samples in the same set. The front phosphorus doped junction is quite good and nearly ideal for solar cell application. The junction depth was 0.21µm with a surface concentration of 2-3 x $10^{19}/cm^3$. The boron doped P^+P junction has a very low surface concentration of 3 x $10^{17}/cm^3$ which would lead to a high resistance back contact. The junction depth of 0.25µm would be satisfactory with a higher surface concentration.

One interesting feature of the data, not yet understood, is the high sheet resistivity of the N^+P junction (Sample 52-2 had a sheet resistance of 300Ω/□) which does not correlate with the spreading resistance data. It is possible that the surface of these samples is somewhat depleted (low C_o → high ρs) but with a higher concentration just below the surface. There is some indication of this buried junction effect in Figure 1.

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* Web used in this sample set had previously been processed using the Westinghouse baseline sequence. These baseline cells gave average efficiencies of 14%.

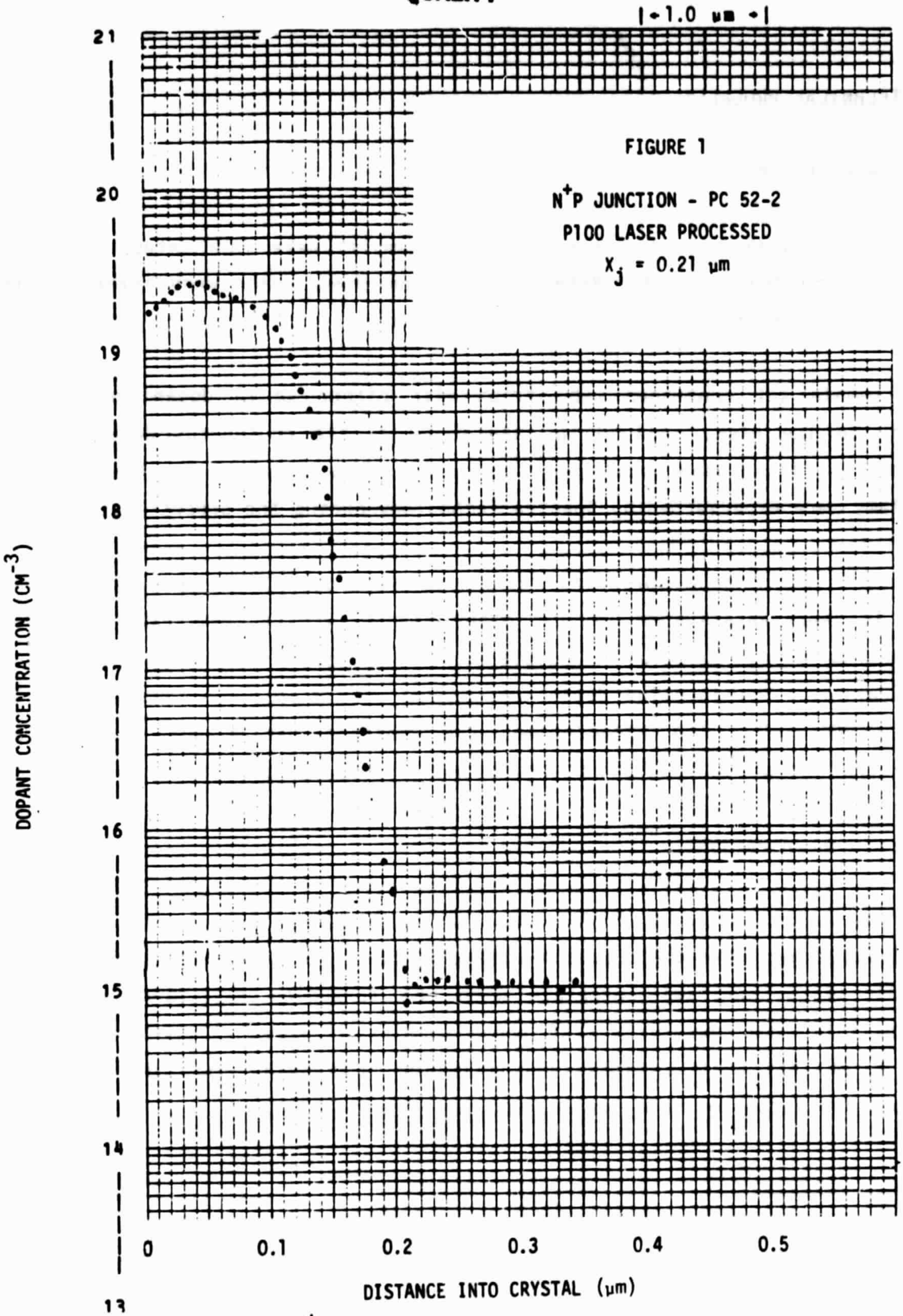

Figure 1. N^+P Junction - PC 52-2 P100 Laser Processed

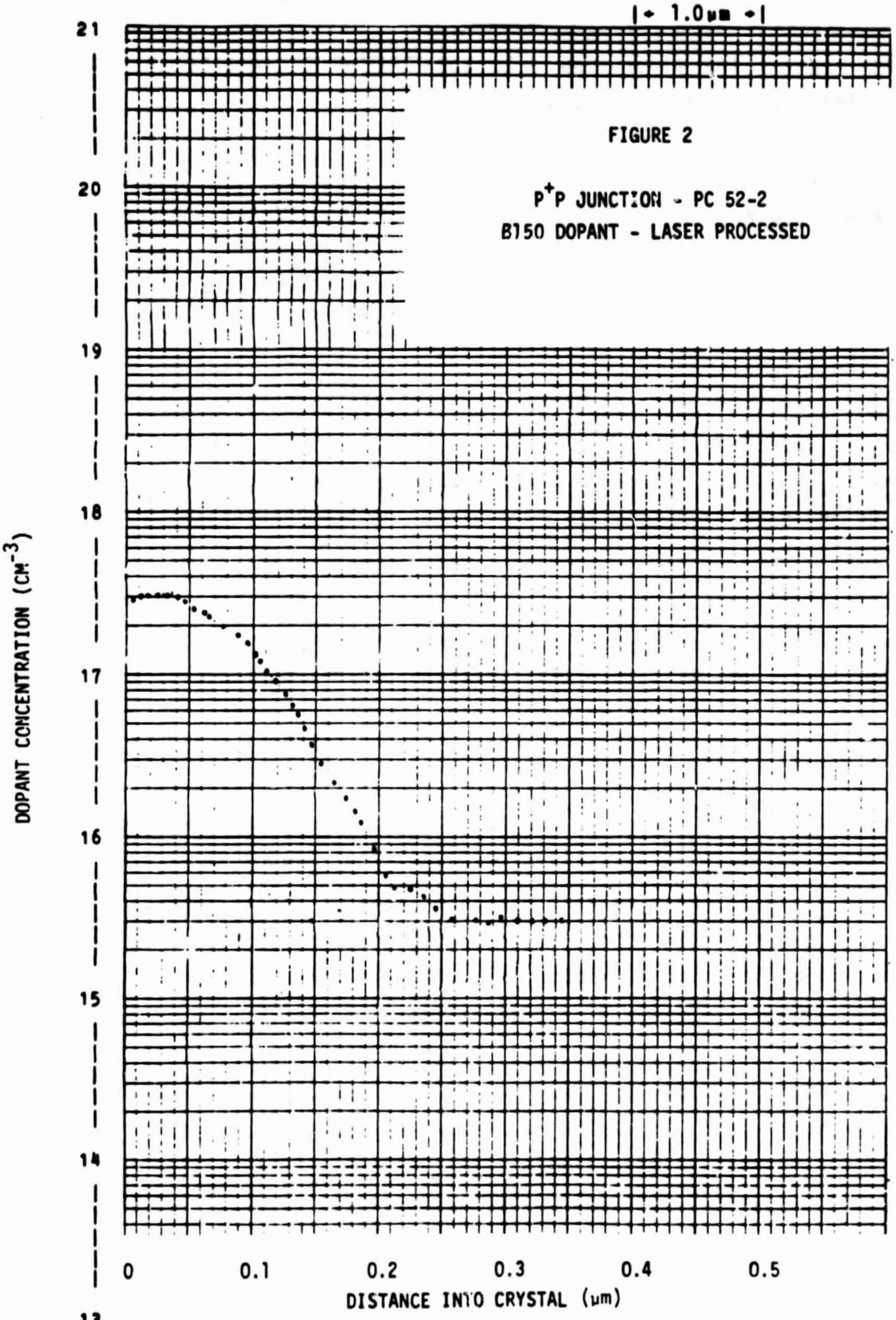

Figure 2. P$^+$P Junction - PC 52-2 B150 Dopant - Laser Processed

Table 1 gives the processing data and lighted IV results on representative cells fabricated from this sample set.

The samples with the Al doped back were poor when no annealing was performed. There was apparently little if any Al driven into the web crystal as indicated by the high sheet resistivity. This was confirmed by spreading resistance measurements which indicated there was no appreciable junction.

When these samples were annealed, the characteristics improved somewhat with a maximum efficiency of 7.8% being achieved with a 700°C anneal. When the back surface was damaged by sandblasting before the anneal, the efficiency increased to 9.2%. This is a further indication of a high series resistance due to the back surface. The cells with the boron doped back junctions showed somewhat better properties, although the sheet resistance was still high. The maximum efficiency of 9.5% (annealed sample) is more than 4% lower than the efficiency of baseline cells on the same web crystal. The efficiency was also increased on two of the sample cells by annealing at 600°C for 1 hour in N_2. However, both the annealed and unannealed cells had a high series resistance, due to the lack of boron penetration into the crystal.

As in the Al doped samples, the efficiency was further increased to a maximum of 10.4% when the back surface was damaged before annealing.

The conclusion drawn from these data is that laser processing as presently carried out is not forming a suitable back junction. The surface concentrations for these P^+ junctions have been uniformly low. This results in a high series resistance back contact and cells with low efficiency. The front contact, however, appears to be quite suitable for solar cell application.

This conclusion is confirmed by the dark IV data shown in Table 2. This data is for three of the cells listed in Table 1. The series resistance is significantly higher than noted on diffused samples where it is normally $<0.5\Omega cm^2$.

TABLE 1
EXCIMER LASER PROCESSING - SAMPLE SET #3

Cell ID	ρs (Ω/□) F	ρs (Ω/□) B	Dopants F	Dopants B	Laser Power (J/cm²) F	Laser Power (J/cm²) B	V_{oc} (V)	J_{sc} (mA/cm²)	FF	EFF (%)	Comments
31-1	330	3K	P100	AL4	2	2	.289	20.1	.29	1.7	
33-1	350	1.5K	P100	AL4	2	2	----	----	----	---	
34-1	300	700	P100	AL4	2	1.5	.432	19.3	.11	1.0	
34-2	350	1.5K	P100	AL4	2	1.5	.373	19.6	.45	3.3	Annealed 1 hr. at 600°C in N_2
35-2	300	85	P100	B150	2	2	.509	24.1	.75	9.3	Annealed 1 hr. at 600°C in N_2
57-1	350	120	P100	B150	2	2	.497	21.3	.60	6.4	
57-2	350	130	P100	B150	2	2	.511	23.8	.78	9.5	Annealed a hr. at 600°C in N_2
59-1	300	100	P100	B150	2	2	.497	21.2	.64	6.7	
59-2	300	100	P100	B150	2	2	----	----	----		Annealed 1 hr. at 600°C in N_2
64-1	300	100	P100	B150	2	2	.511	24.2	.70	8.7	
64-2	300	100	P100	B150	2	2	.515	24.4	.73	9.2	Annealed 1 hr. at 600°C in N_2
42-1	300	600	P100	AL4	2	1.5	.494	21.4	.73	7.8	Anneal 700°C 1 hour
42-2	350	1000	P100	AL4	2	1.5	.513	25.4	.70	9.2	Damage back and anneal 700°C 1 hour
52-2	260	90	P100	B150	2	2	.517	24.7	.75	9.6	Anneal 700°C 1 hour
63-2	300	100	P100	B150	2	2	.527	25.4	.78	10.4	Damage back and anneal 700°C 1 hour

NOTES:

1. AL4 - Allied Chemical - Metallorganic Precursor Containing Aluminum
2. B150 - Allied Chemical - Metallorganic Precursor Containing Boron
3. P100 - Allied Chemical - Metallorganic Precursor Containing Phosphorous
4. Where no test data is given the cell had essentially zero voltage.
5. All cells AR coated.

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TABLE 2

DARK IV DATA - LASER PROCESSED CELLS

Cell ID	Voc (V)	Jsc (mA/cm^2)	Eff (%)	J01 A/cm^2	J02 (A/cm^2)	Rs ($\Omega\ cm^2$)	Rsh ($\Omega\ cm^2$)	Ln (μm)
42-1	.494	21.4	7.8	7.1E-11	1.8E-5	1.2	1.8K	30
42-2	.513	25.4	9.2	4.0E-11	1.4E-5	1.4	2.6K	45
63-2	.527	25.4	10.4	2.4E-11	2.2E-6	0.6	10.9K	30

Diffusion length (Ln) measured by surface photovoltage.

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C.2 Junction Formation by Pulsed Directed Heating

A novel method for junction formation was devised and several experiments were carried out during this period. In this technique, the dopants are applied to both sides of the web and the strip is subjected to a high temperature-short term heating cycle from a tungsten-halogen flash lamp.* Figure 3 (supplied by AG Associates) shows a typical heating cycle of 1100°C for 15 seconds.

There are several distinct advantages to this technique. First, the junction formation is rapid, taking less than 1% of the normal time. This reduces processing time and energy costs. Second, both junctions can be diffused simultaneously; and due to the short time period that the Si is at a high temperature, cross-contamination of the dopants should not occur.

Table 3 shows the results of conductivity and sheet resistance measurements made on the first set of samples processed using the pulsed heating technique. The sheet resistivity of the front surface (phosphorus doped) is considerably lower than the 60Ω/□ specified for the baseline sequence, while the back sheet resistivity is high. This would be expected since phosphorus diffuses nearly a half an order of magnitude faster than boron at 1100°C.

Figures 4 and 5 show the front and back junctions for sample #16. The junction depths of 0.15μm and 0.10μm for the N^+P front and the P^+P back junctions are in fair agreement with the depths calculated for a 15 sec. - 1100°C diffusion. The surface concentrations ($7 \times 10^{20}/cm^3$ for the N^+ surface and $2 \times 10^{20}/cm^3$ for the P^+ surface) are higher than those obtained using the baseline diffusion process. This may be an effect of the very short diffusion time. Somewhat lower concentrations are preferred for high efficiency cells.

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*The diffusions were performed courtesy of AG Associates, Palo Alto, CA.

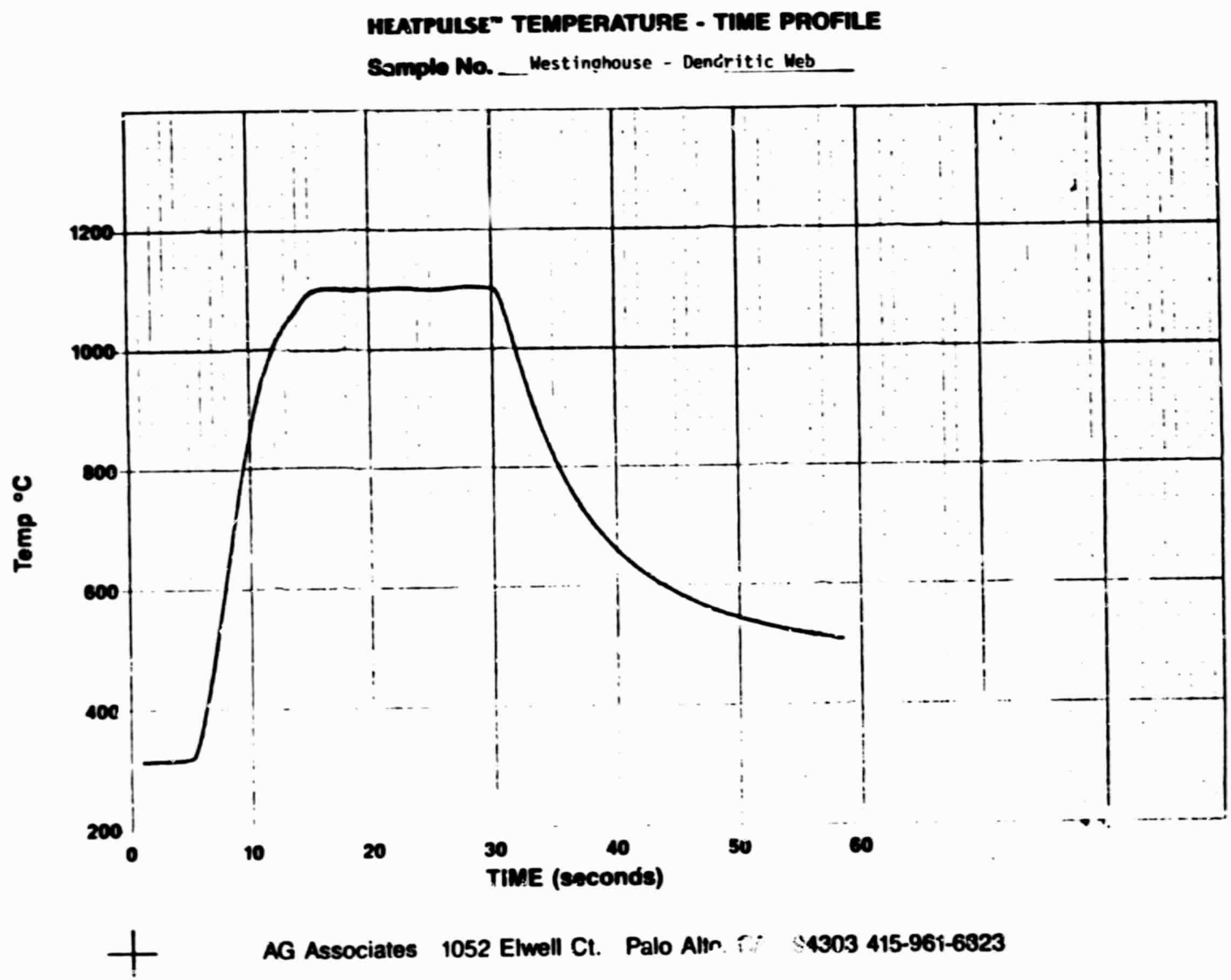

Figure 3. Typical Heating Cycle for Short Time-High Temperature Diffusion

TABLE 3

CONDUCTIVITY AND SHEET RESISTIVITY MEASUREMENTS
ON HEATPULSE* FORMED JUNCTIONS

	Conductivity		Sheet Resistivity (Ω/□)	
Sample	Front	Back	Front	Back
16	N	P	16	63
19	N	P	24	62
20	N	P	27	80
25	N	P	27	80

NOTES: 1. The junctions were diffused simultaneously.

2. There was no evidence of any cross-contamination as measured by conductivity probing.

*TM - AG Associates

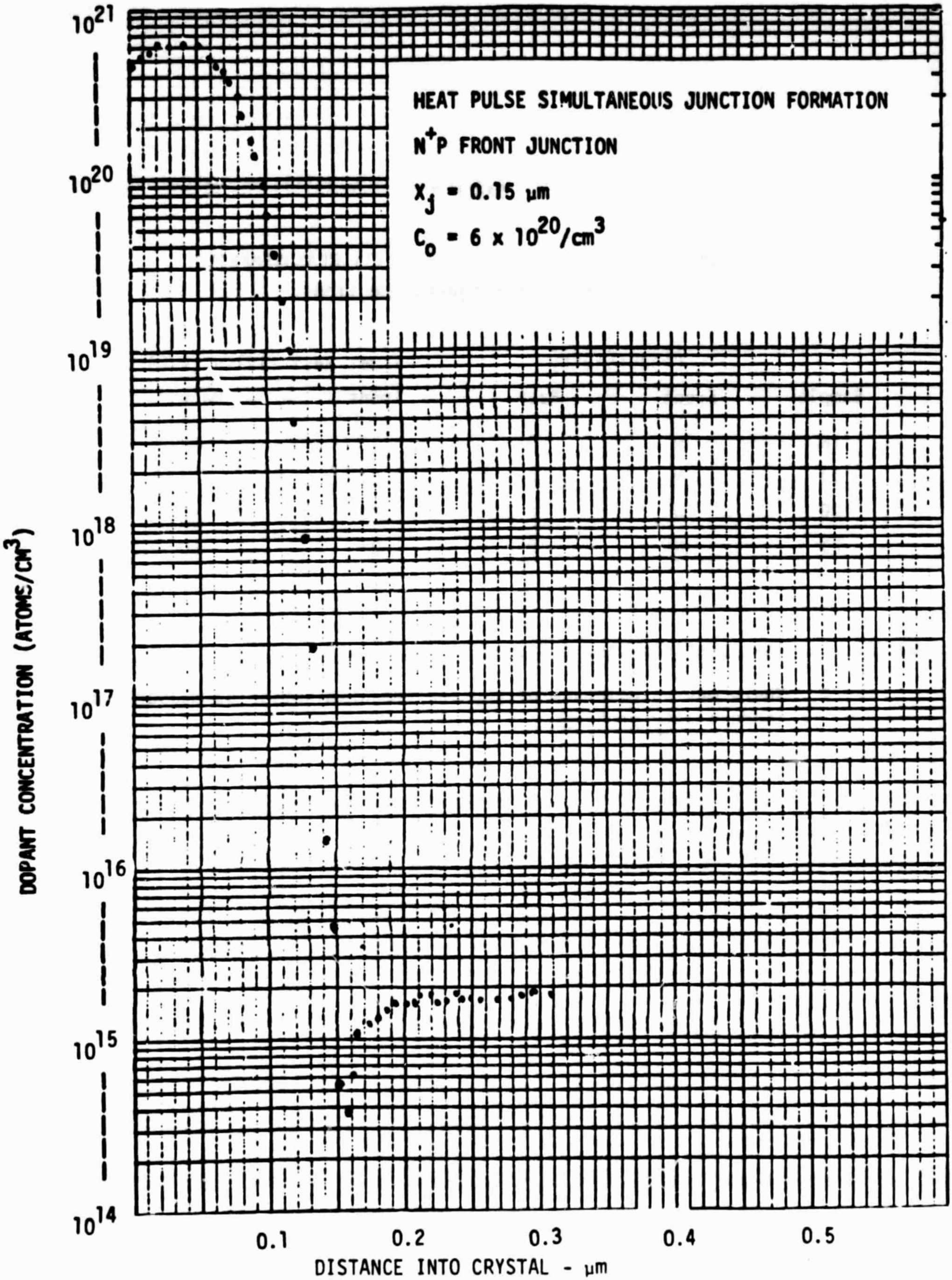

Figure 4. Front N^+P Junction Formed by Short Time-High Temperature Diffusion

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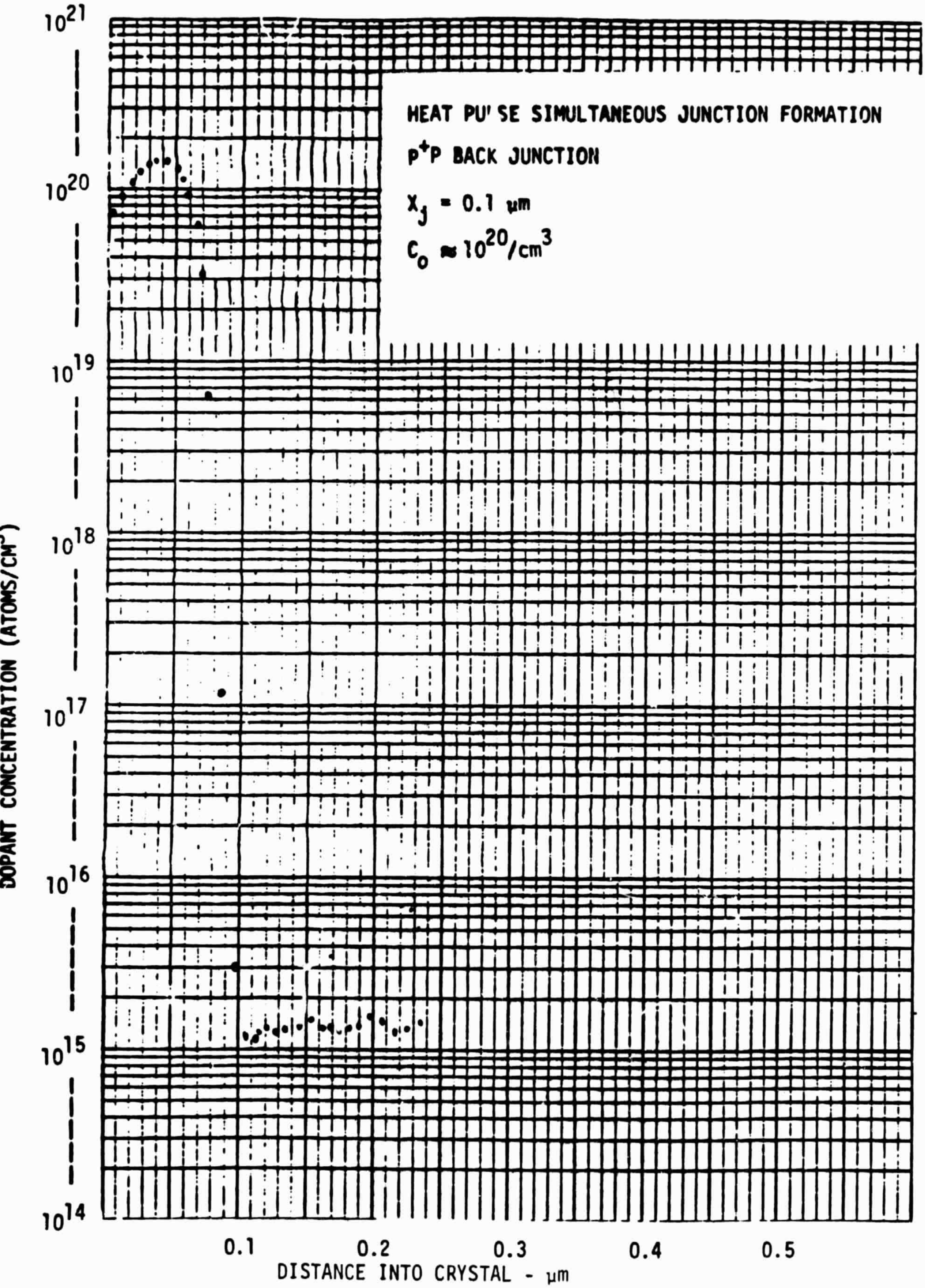

Figure 5. Back P^+P Junction Formed by Short Time-High Temperature Diffusion

Cells have been processed from a number of these samples. When the cells were fabricated on the as-diffused samples, the efficiency was lower than that obtained with the baseline process (diffusion at lower temperatures).

Rapid cooling from the diffusion temperature (as occurs in the pulsed directed heating method) will give rise to quenched-in defects. These defects may be vacancy clusters, dislocations, etc., which may or may not be decorated with impurities. These defects or their effects can be partially or wholly removed by various annealing treatments. This annealing may also assure that the dopants are in their proper substitutional lattice sites.

Table 4 gives Lighted IV data measured on a number of cells fabricated on web where the junctions were simultaneously formed by the pulsed directed heating technique.

Several points should be noted from data presented in this table.

First, annealing is required for these samples if a high efficiency cell is to result. The highest efficiency obtained on the unannealed sample was 9.4% for the P base cells and 11.8% for the N base cells. This validates the comments made regarding the quenched in defects due to rapid cooling.

Second, high efficiency cells can be obtained using this junction formation method with maximum efficiencies of 13.0% for the P base cells and 15.2% for the N base cells. At this point there is no explanation for the generally higher efficiencies obtained on the N base material.

Third, although further optimization is required, annealing temperatures approximately 800°C are required. If the annealing is carried out above 800°C, the time must be reduced to prevent diffusion of the dopant species.

Table 5 shows dark IV data on three cells with junctions formed by the directed heating.

TABLE 4

LIGHTED IV DATA - CELLS FABRICATED ON WEB WITH JUNCTIONS FORMED BY PULSED DIRECTED HEATING

Cell ID	Bulk Cond.	Bulk Res. (Ω cm)	Voc (V)	Jsc (mA/cm^2)	FF	Eff (%)	Comments
1A	P	4	.065	24.3	.23	1.3	No anneal
1B	P	4	.518	27.1	.75	10.5	900°C - 1 hr
8A	P	4	.497	23.8	.76	9.0	No anneal
8B	P	4	.541	29.1	.78	12.3	800°C - 1 hr
10A	P	4	.537	30.0	.77	12.4	800°C - 1 hr
10B	P	4	.529	26.0	.76	10.5	900°C - 1 hr
12A	P	4	.511	23.6	.78	9.4	No anneal
12B	P	4	.521	27.9	.76	11.0	800°C - 1 hr
61A	P	4	.455	15.8	.77	5.6	No anneal
61B	P	4	.485	17.2	.77	6.4	700°C - 1 hr
66A	P	4	.482	21.0	.47	4.8	800°C - 1/2 hr
66B	P	4	.533	27.3	.77	11.1	900°C - 1/2 hr
49A	P	4	.556	29.3	.79	13.0	850°C - 1/2 hr
49B	P	4	.526	25.5	.75	9.9	700°C - 1 hr
6A	N	1	.556	24.9	.69	9.6	No anneal
6B	N	1	.578	30.5	.75	13.2	800°C - 1 hr
7A	N	1	.561	26.6	.79	11.8	No anneal
7B	N	1	.601	32.9	.77	15.2	800°C - 1 hr
81A	N	1	.560	25.5	.79	11.3	No anneal
81B	N	1	.600	32.2	.78	15.1	800°C - 1 hr
85A	N	0.5	.587	30.5	.79	14.9	700°C - 1 hr
87A	N	1	.583	32.3	.79	14.9	900°C - 1 hr
88A	N	1	.593	32.2	.79	15.0	900°C - 5 min
88B	N	1	.581	29.8	.78	13.5	800°C - 1/2 hr

NOTES: 1. After annealing samples were cooled at 2-3°C/min.

2. The samples noted as A and B were from the same web crystal.

Of special note in Table 5 is the very high diffusion length of cell 7B, which correlates with the high efficiency (15.2%). The bulk saturation current of the P base cells is significantly higher (by an order of magnitude) than the N base cell. This could account for the lower diffusion length ard efficiency.

From these initial experiments, it is concluded we conclude that simultaneous junction formation using pulsed directed heating is a promising technique. In addition to the rapidity of the junction formation, the cell efficiency (at least for the N base cells) is enhanced.

Further work is required to optimize the junction formation time and temperature as well as annealing conditions.

TABLE 5

DARK IV DATA - CELLS FABRICATED ON WEB WITH JUNCTIONS FORMED BY PULSED DIRECTED HEATING

Cell ID & Treatment	Bulk Cond.	Voc (V)	Jsc (mA/cm^2)	η (%)	Rs ($\Omega\ cm^2$)	Rsh ($\Omega\ cm^2$)	J01 (A/cm^2)	J02 (A/cm^2)	Ln (μm)
13A 900°C-1 Hr	P	.521	26.1	10.7	.7	132K	3E-11	4.9E-7	32
8B 800°C-1 hr	P	.541	29.1	12.3	.7	25K	1.4E-11	1.5E-6	48
7B 800°C-1 hr	N	.601	32.9	15.2	.7	.5K	1.5E-12	4.13-5	350

Diffusion length (Ln) measured by surface photovoltage.

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D. PROBLEMS

Laser Processing - Shallow penetration of boron leading to high resistivity back surface (P base cells) or poor emitter (N base cells).

Pulsed Directed Heating - Need to optimize diffusion and annealing conditions. Must also investigate reasons for lower efficiency in P base cells. This work is beyond the scope of the existing contact.

E. PLANS

1. Further cell fabrication of web with junction formed by pulsed directed heating.

2. Prepare final report.

3. Format A's will be submitted with the final report.

F. Figure 6 is a graphic presentation of the program tasks and scheduled completion dates.

TASK	J	F	M	A	M	J	J	A
1. INVESTIGATE LASER DRIVE-IN OF LIQUID DOPANTS					Δ			
2. CONDUCT SENSITIVITY STUDIES							Δ	
3. SUBMIT FORMAT A'S						Δ		
4. SAMPLE CELLS AND MATERIAL		Δ		Δ		Δ		
5. FINANCIAL MANAGEMENT REPORTS	▲	▲	▲	▲	▲	Δ	Δ	
6. MONTHLY TECHNICAL REPORTS	▲	▲		▲	▲		Δ	
7. QUARTERLY REPORTS			▲			▲		
8. DRAFT OF FINAL REPORT								Δ

Figure 6. Process Research of Non-CZ Silicon Material Milestone Chart - Contract 956616 Mod. 1